

# Humic acids removal by aerated spiral-wound ultrafiltration membrane combined with coagulation–hydraulic flocculation

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## ARTICLE INFO

### Article history:

Received 23 April 2010

Received in revised form 10 August 2010

Accepted 10 August 2010

### Keywords:

Humic acids

Hydraulic flocculation

Aerated spiral-wound ultrafiltration

membranes

Trihalomethane

## ABSTRACT

An aerated spiral-wound ultrafiltration membrane system (ASWUF) combined with coagulation–hydraulic flocculation was tested with a view to evaluating its efficiency as a system for removing humic acids (HA). The tests were carried out at pilot scale, using  $\text{FeCl}_3$  as a coagulant. The ASWUF was equipped with polyethersulphone membranes (molecular weight cut-off of 50 kDa). The system was fed with reservoir water, to which different concentrations of HA (1–30 mg/l) were added. HA removal capacity of the ASWUF varied according to the molecular weight (MW) of the HA, and performance never exceeded 41% as dissolved organic carbon (DOC). However, coagulation–flocculation combined with ASWUF achieved results of approximately 90% for HA concentrations of up to 30 mg/l. Coagulation–flocculation as pretreatment for ASWUF makes it possible to remove HA with a low MW, without having to modify the pH of the water. This efficiency led to a decline in the specific UV absorbance (SUVA) of the effluent, which therefore presented a lower risk of trihalomethane (THM) generation after post-chlorination. Final effluent HA concentration was the main conditioning factor for THM generation. However, it was noted that the fraction of HA persisting after treatment generated a higher concentration of THM per unit of DOC.

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## 1. Introduction

Chlorination of drinking water is a very widespread practice thanks to its versatility in controlling the propagation of infectious diseases through the consumption of water. However, the generation of disinfection by-products (DBPs) during chlorination has led scientists to search for new strategies in water treatment, including the elimination of precursors of DBP generation, such as natural organic matter (NOM).

Aquatic NOM is a heterogeneous mixture of organic compounds which vary in terms of molecular weight (MW), chemical structure and functional groups. NOM is often fractionated on the basis of hydrophobicity and molecular size [1] and therefore includes a set of hydrophilic substances, particularly aliphatic carbon and nitrogenous compounds (sugars, carbohydrates, amino acids etc.), and a set of hydrophobic substances, consisting principally of humic compounds (humic and fulvic acids), noted for their aromaticity and carboxylic and phenolic acid functionality.

Of these substances, hydrophobic NOM compounds have been catalogued as the main precursors of the appearance of DBPs after chlorination of the water [2,3]. At the same time, hydrophobic NOM

generates problems of colour, odour and taste, making water treatment necessary. The compounds with the greatest MW in this group are humic acids, which also represent the largest fraction of NOM and are of allochthonous origin [4].

Various strategies may be used to eliminate NOM from water, and techniques such as adsorption on activated carbon, chemical oxidation and membrane processes have been proposed as viable alternatives [5]. According to Siddiqui et al. [6] and Hyung and Jin [7], nanofiltration membranes offer the best option for eliminating NOM from water, particularly the compounds with the greatest molecular weight. However, nanofiltration membranes require pretreatment since they have continual problems with fouling and clogging and are subject to serious operational difficulties such as reduced recoveries or high transmembrane pressure [6].

Other types of membrane such as microfiltration membranes are incapable of eliminating NOM, or show only limited capacity, as in the case of ultrafiltration membranes. However, the combination of micro- or ultrafiltration membranes with nanofiltration membranes is highly efficient [6,7], owing to the effectiveness of nanofiltration membranes at eliminating NOM, while the pretreatment membranes prevent operational problems through the efficient removal of particulate material.

Coagulation is proposed by the USEPA as an effective method for removing DPB precursors during the water treatment process [8]. The efficiency of this method depends on the dose and type of coagulant

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With these considerations in mind, the aim of the present study was to apply an ultrafiltration membrane system to eliminate humic acids (HA) from water. The experimental system was equipped with a pretreatment system based on coagulation–hydraulic flocculation in order to achieve higher removal capacities. The study uses potential formation of trihalomethanes (THM) after the process as an analytical method for evaluating the efficiency of the system.

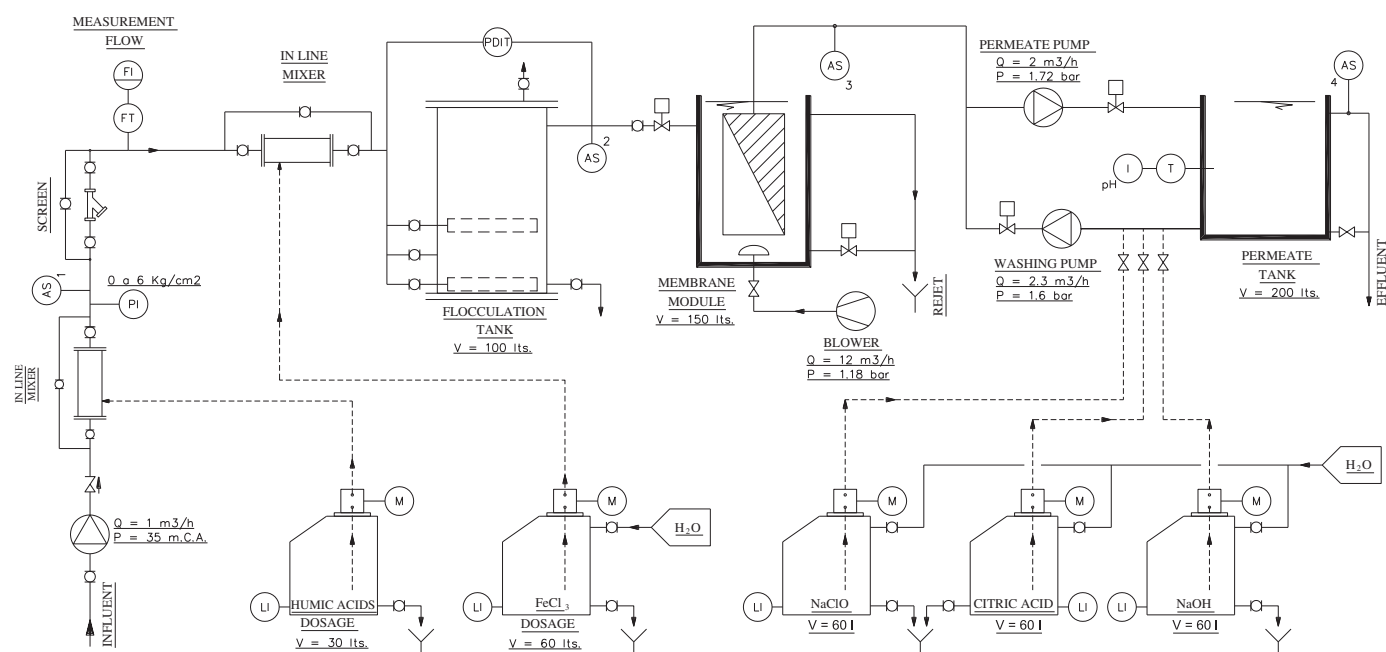
### 2.1. Pilot scale installation

## 2.2. Influent characteristics

Water was sourced from the Canales reservoir in the province of Granada (Spain). The main characteristics of the water were as follows: pH 8.03; conductivity 206  $\mu\text{S}/\text{cm}$ ; turbidity 6.4 NTU; DOC 0.4 mg C/l;  $\text{UV}_{254 \text{ nm}}$  0.2  $\text{m}^{-1}$  and  $\text{Br}^- < 0.01 \text{ mg/l}$ . A suspension of humic acids (HA) (Aldrich Chemicals, Milwaukee) was continuously added to the influent, prepared in pure water (Milli-Q, Millipore Corp.) at a concentration of 100 mg/l. The dosing pump was adjusted to obtain HA concentrations of between 5 and 30 mg/l in the influent. The main characteristics of the water with added HA are shown in Table 1.

### 2.3. Experimental procedure

In the second phase,  $\text{FeCl}_3$  was used as the coagulant and the dose was adjusted depending on the quality of the influent (by Jar Test). Similarly, the velocity gradient ( $G$ ) of the hydraulic flocculator was adjusted to ensure a constant retention time ( $\text{HRT} = 6.6 \text{ min}$ ), in order to obtain flocs which could be easily separated by the ultrafiltration



**Fig. 1.** Schematic diagram of experimental pilot plant.

**Table 1**  
Characteristics of the water from Canales reservoir with different HA concentrations.

HA (mg/l)	pH	mg DOC/l	UV <sub>254</sub> m <sup>-1</sup>	Turbidity (NTU)
0	8.04	0.4	0.2	6.4
5	8.00	4.6	5.2	7.8
10	7.98	7.2	18.0	10.7
20	7.90	12.9	66.4	16.3
30	7.88	17.2	90.5	19.3

membrane without causing clogging problems, as described in previous experiments by Rojas et al. [11].

#### 2.4. Analytical methods

In order to determine the molecular weight (MW) of the humic acids, we had first to fraction them by means of centrifugal ultrafiltration of an HA solution (30 mg/l) carried out on the influent. Filters with the following nominal molecular weight cut-offs were used: 3 kDa, 10 kDa, 30 kDa, 50 kDa and 100 kDa (Amicon, Millipore Corp., Bedford MA). Prior to separation, ultrafilters were soaked in 30% methanol/70% water (v/v) to remove leachable organic carbon. After soaking, five aliquots of water were processed. Absence of organic material was tested using the total organic carbon (TOC) analysis on the final aliquot. Centrifugation was performed at 4000 rpm for 10 min over a volume of 15 ml and filtrates were collected and analysed for TOC.

An analysis of chlorine demand was carried out for the different concentrations of HA in the experimental plant. A solution of hypochlorite (1 g Cl<sub>2</sub>/l) was added to 1 l of sample, in accordance with the demand observed. Subsequently, gentle stirring (30 rpm) was maintained for a period of 24 h in darkness and at a constant temperature of 25 °C. The water was sampled every hour to determine the presence of residual chlorine by means of the *N,N*-diethyl-*p*-phenyldiamine ferrous titrimetric method [12]. Chlorine demand was calculated by subtracting the residual chlorine from the chlorine added.

The influent and effluent of the experimental plant were sampled for DOC and UV<sub>254</sub> analysis. Water samples were collected daily in thoroughly cleansed plastic bottles and analysed immediately. Prior to analysis, samples were filtered through 0.45 µm membranes. For the determination of UV<sub>254</sub> nm absorbance, a UV-visible spectrophotometer was used (Helios γ) with a 1 cm quartz cell. TOC and DOC were measured using a combustion TOC Analyser (SKALAR, Formacs<sup>TH</sup>). Specific UV absorbance (SUVA) was calculated as UV<sub>254</sub> × 100/DOC (mg/l).

Trihalomethane formation (THMF) test was based on the uniform formation conditions protocols described by Summers et al. [13]. Experiments were conducted at the pH of natural waters samples and different chlorine concentrations (5 to 30 mg Cl<sub>2</sub>/l) were added to 100 ml of sample in a brown glass bottle, which was filled completely and hermetically sealed. The reaction was maintained in darkness for 24 h at 20 °C, after which residual chlorine was eliminated through the addition of a stoichiometric quantity of NaHSO<sub>3</sub>. THM concentrations were determined by purge and trap gas chromatography with electron capture detection (Thermo Instrument Systems Inc, California USA), together with a mass spectrometer (Micromass International Ltd, Manchester UK).

#### 2.5. Statistical analysis

All data obtained in the study were analysed using the statistical program STAGRAPHS Plus 3.0 for Windows. For each assay, influent DOC and UV<sub>254</sub> were compared with those of the effluent, and the corresponding linear correlation coefficients were obtained in each case. A similar comparison was undertaken for SUVA values. Values

obtained in the chlorination assays were adjusted to the best possible mathematical regression.

### 3. Results and discussion

#### 3.1. Molecular weight distribution of humic acids

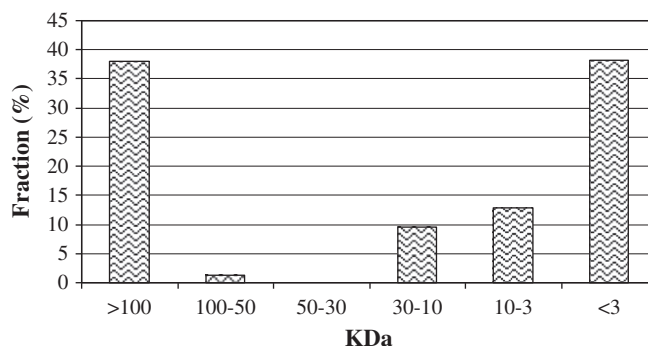
In order to evaluate the efficiency of the ASWUF system at removing HA, we had to calculate the molecular weight distribution of the HA (Fig. 2). Approximately 40% of the humic acids presented an MW above the cut-off for the ultrafiltration system we used (50 kDa). The remaining HA were below this figure, and 38% had an MW of less than 3 kDa. This molecular weight distribution was similar to that observed by Kim and Yu [14] in the Han River (Korea). However, natural water has a lower molecular weight distribution with nearly all the HA under 3 kDa [4,15]. When used alone, the ASWUF system is only able to eliminate the HA fraction above its cut-off point, as its main action mechanism is essentially one of screening or sieving. This means that the HA fraction with an MW below the membrane cut-off point, the predominant fraction in natural waters, passes through the membrane easily.

#### 3.2. ASWUF assays

As may be expected given the gradation of HA, the average performance of the ASWUF system applied as a single treatment for the elimination of NOM was 41% measured as DOC, and 46% measured as UV<sub>254</sub>. It is significant that as the concentration of HA increased in the influent, it also increased in the effluent (Fig. 3), with a high linear correlation between the influent and effluent concentrations, measured in terms of both DOC and UV<sub>254</sub> ( $r^2 = 0.9978$  and  $r^2 = 0.9967$  respectively). Bearing in mind that 60% of the HA added to the influent had MW of under 50 kDa, these must have penetrated the membrane through the pores, thus explaining the correlation between influent and effluent concentration levels.

Previous experiments carried out by Rojas et al. [10] achieved similar performance levels for water with a low concentration of NOM. In general, however, yields have been lower, at around 30% [6,7], similar to those achieved by conventional water treatment systems [7]. Clearly, inefficient NOM removal is one of the chief drawbacks of ultrafiltration membranes, and limits their application as the main process in water potabilization, in spite of their excellent capacity for physical disinfection [10].

The chlorination assays carried out on the HA revealed a high chlorine demand, with average values of 4.3 mg Cl<sub>2</sub>/mg DOC. Oxidation was relatively rapid, with a high consumption in the initial hours followed by a gradual decline. The data obtained correspond to a Square root-X model regression, with at least 24 h being required for the oxidation of concentrations of up to 10 mg/l of HA, as indicated in Fig. 4. This chlorine demand is relatively high when compared to



**Fig. 2.** Molecular weight distribution (by DOC) of humic acids used in the study.

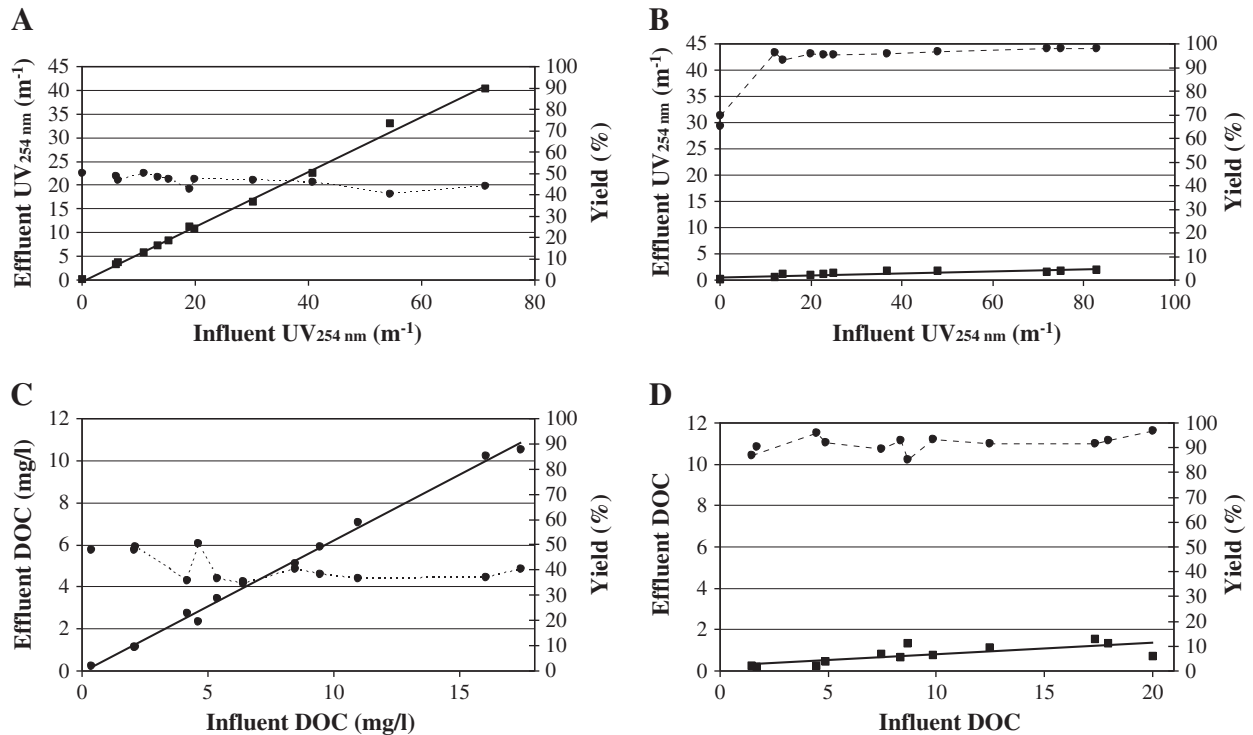


Fig. 3. Influent and Effluent NOM correlation for ASWUF without (A and C) and with (B and D) previous coagulation–flocculation. (■)  $m^{-1}$ , (●) yield.

values found in natural water samples, as reported by Fabris et al. [4]. These authors observed that water with a higher presence of HA has a greater chlorine demand than water with a higher hydrophilic component. Accordingly, ASWUF treatment of water with a high content of HA would produce effluents with a high chlorine demand, thus causing problems of microbiological contamination in the water distribution network, owing to the lack of free residual chlorine and the presence of organic material. There would also be a serious risk of by-products such as THM [3] being generated in the distribution network.

### 3.3. Coagulation–flocculation/ASWUF assays

The coagulation–flocculation system required a continual adjustment of both the dose of  $FeCl_3$  and the flocculator velocity gradient depending on the concentration of HA, in order to maintain the TMP [11]. Once this had been achieved, the system was put into continuous operation taking into account the specific characteristics of the influent.

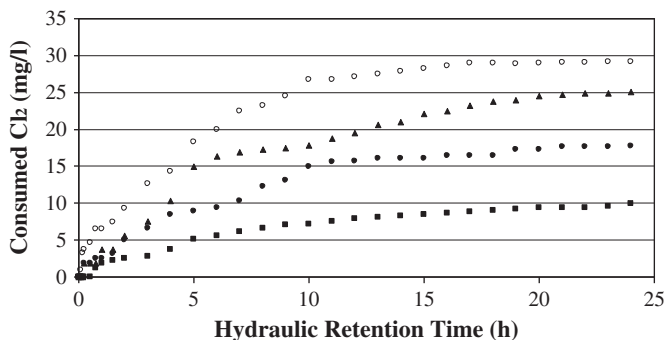


Fig. 4. Chlorine demand for humic acids. (■) 5 mg/l; (●) 10 mg/l; (▲) 20 mg/l; (○) 30 mg/l.

A significant improvement was observed in the capacity for removing HA, with values of over 90% being achieved (Fig. 3), without having to modify the pH of the water. There was also a notable decrease in the correlation between the HA concentration in the influent and the effluent ( $r^2 = 0.539$  for DOC and  $r^2 = 0.7475$  for  $UV_{254}$ ), indicating that the system was also efficient at removing HA with low MW.

For pH values such as those found in the water being treated, one of the principal action mechanisms of both the Fe and the Al coagulants is the adsorption and co-precipitation of HA by the corresponding hydroxide [9,16]. This occurs principally in the case of HA with higher MW [16]. However, the performance levels achieved by the experimental system indicate that HA that were not retained through simple screening were also affected. According to Zhao et al. [16], coagulation of HA with low MW using coagulants such as  $Al^{3+}$  takes place due to charge neutralization at pH values of around 5.5. However, in the present experimental conditions this phenomenon would not occur, which means that these types of compound must be removed by some other mechanism.

In a continually operating system, the screening process results in the formation of cake on the membrane surface due to the accumulation of retained material. This accumulation may cause an increase in the TMP and lead eventually to the clogging of the system, due particularly to the accumulation of particles between 0.1 and  $1.5 \mu m$  [17]. However, according to studies by Xia et al. [18], the application of coagulation–flocculation may lead to the formation of cake which not only increases the retention capacity of the membrane, but also prevents particles which cause clogging from reaching the membrane.

We can therefore state that the ASWUF system combined with coagulation–flocculation facilitates the elimination of HA from the water, without having to modify the pH. At the same time, membrane clogging is avoided, since the cake formed on the membrane may be dispersed easily through backwashing. This means that the system can be applied to water with a high concentration of HA, despite the fact that these types of compound have been considered the principal cause of fouling and clogging in ultrafiltration membranes [19].

### 3.4. SUVA

The SUVA seems to be clearly correlated with the aromatic content of NOM. However, it should be noted that the increase in the concentration of the HA caused an increase in the SUVA value, even though the same type of compound was added. This was due to the fact that the DOC increased in a linear fashion with respect to the concentration of HA, while the  $UV_{254}$  showed a multiplicative increase, as can be observed from the data in Table 1. This means that the SUVA value rose in line with the increase in HA concentrations.

Fig. 5 shows the evolution of SUVA in the ASWUF system. As may be seen, when the membrane is used as the sole treatment, there is a linear correlation between influent and effluent values. In this case, it is noticeable that in spite of the fact that the system eliminates some HA, the SUVA value in the influent is very similar to that of the effluent, with a linear regression slope of approximately 1. Application of coagulation–flocculation brought about a decrease in the concentration of HA, and this in turn caused a significant reduction in the SUVA value, with no appreciable correlation between the influent and effluent. Bearing this in mind, it may be that a different response to  $UV_{254}$  absorbance takes place depending on the MW of the HA, with those with low MW showing greater aromaticity. Johnson et al. [20] observed a varying UV response dependent on MW in Aldrich HA, with a greater SUVA for fractions between 2 and 10 kDa, while fractions below and above this weight presented lower SUVA values. This would explain the results obtained in the experimental system, although previous authors have described other patterns of behaviour, suggesting that the relationship between SUVA and MW varies according to the source [20].

These results indicate that the ASWUF system is capable of eliminating HA with greater MW, while fractions with low MW remain in the effluent, principally those between 2 and 10 kDa, which show a greater  $UV_{254}$  response. Consequently, the SUVA values in the influent and effluent are similar. By contrast, previous application of coagulation–flocculation to the membrane reduces the presence of HA

between 2 and 10 kDa, which means there is a decrease in the SUVA values in the effluent.

As Archer and Singer [21] noted, SUVA is a valuable parameter when evaluating NOM reactivity and treatability. According to the SUVA values in this experiment, the ASWUF system used alone provides an effluent with a high residual concentration of HA, with a correspondingly high risk of THM generation when disinfectants such as chlorine are applied. However, application of coagulation–flocculation in combination with the ASWUF system brings about a decrease both in the concentration of organic material and in the potential generation of THM. Post-chlorination could therefore be used to prevent microbial contamination in the distribution network, since the reduction in HA concentration leads to a decrease in chlorine demand and thus minimizes the risk of THM generation.

### 3.5. Trihalomethane generation

The application of different concentrations of chlorine to the effluent shows that after 24 h in contact with the chlorine, water treated by ASWUF alone had generated more THMs than water treated by the coagulation–flocculation/ASWUF combination (Fig. 6). This is clearly due to the differing performance of the two systems with regard to HA elimination. Nevertheless, the concentration of the THM generated was dependent on the concentration of the chlorine added to the water as well as on the HA concentration. For assays with 30 mg/l of HA (17.2 mg DOC/l), the ASWUF system produced an effluent with 10 mg DOC/l. On the basis of the earlier chlorination tests, this would require approximately 43 mg  $Cl_2$ /l for total oxidation. Assays at this level generated the greatest concentration of THM, which increased in accordance with the increase in the dose of chlorine, reaching values of 301  $\mu$ g/l of THM for chlorine doses of 30 mg  $Cl_2$ /l. This contrasts with assays with HA concentrations of 5 mg/l (4.63 mg DOC/l), which produced an effluent with a final concentration of 2.3 mg DOC/l after treatment by ASWUF. In this case, total oxidation would be obtained by a concentration of 9.89 mg  $Cl_2$ /l. For tests at 5 mg/l of HA, the greatest concentration of THM was 31  $\mu$ g/

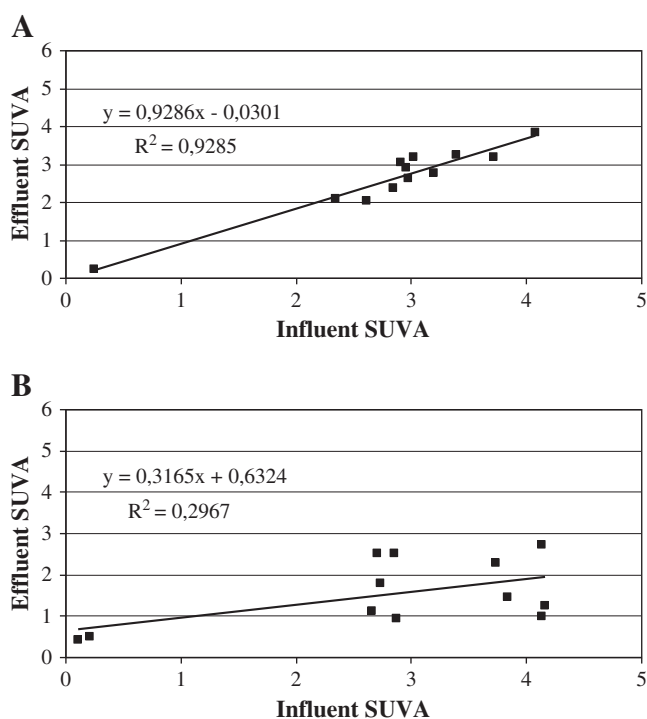


Fig. 5. Influent and effluent SUVA correlation for ASWUF without (A) and with (B) previous coagulation–flocculation.

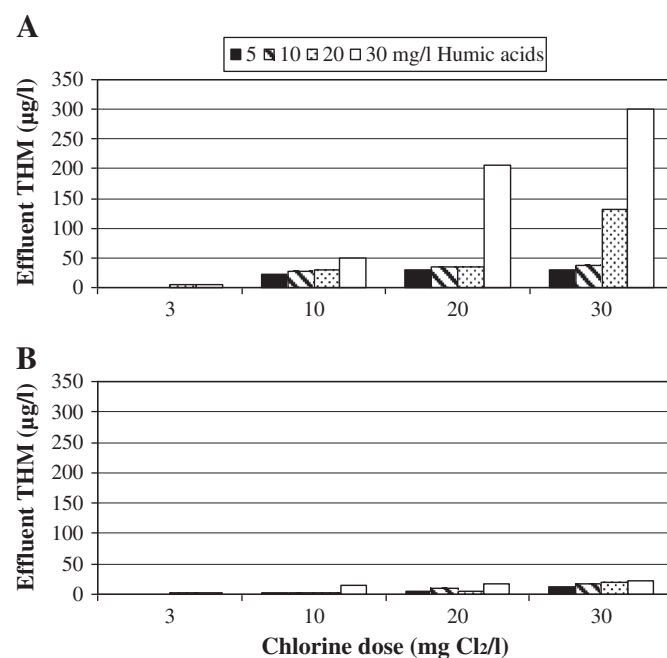


Fig. 6. Effluent THM concentration after chlorination (3–30 mg  $Cl_2$ /l) after ASWUF without (A) and with (B) previous coagulation–flocculation treatment of influent with different humic acid concentrations.

l for a chlorine dose of 30 mg  $\text{Cl}_2/\text{l}$ . As may be seen, while the concentration of chlorine added to the water is a determining factor for the generation of THM, as shown in Fig. 6, the concentration of HA has greater impact, because it determines the demand for chlorine in the water. Specifically, the incomplete oxidation of high concentrations of HA leads to the generation of more by-products.

The presence of HA was drastically reduced by the coagulation–flocculation/ASWUF combination, with a corresponding decrease in the demand for chlorine. This enables the total oxidation of the HA remaining in the water with low doses of chlorine, thus reducing the presence of THM, which never rose above concentrations of 23  $\mu\text{g/l}$ .

The post-chlorination THM concentrations were similar to those observed by Krasner et al. [22] for water with low presence of  $\text{Br}^-$  and an almost exclusive predominance of  $\text{Cl}_3\text{CH}$ , as was the case in our experiment. However, the concentrations appear significantly low alongside the chlorine doses and NOM concentrations observed by Fabris et al. [4], when working with natural water in different areas of the planet. This leads us to suppose that while HA is a major precursor of THM generation, there are other components of NOM that may play a more important role.

In order to assess the reactivity of the HA present in the water, the THM values obtained after adding the maximum concentration of chlorine (30 mg  $\text{Cl}_2/\text{l}$ ), on the basis of the DOC concentration in the chlorinated sample, were considered as a measure of potential THM generation (THMP). Values obtained in the influent and effluent were then compared (Fig. 7). Results show greater THM generation per gram of DOC in the effluents than in the influents, while the effluents obtained after application of the coagulation–flocculation/ASWUF combination showed the highest THM generation. The fraction of HA remaining after the treatment thus appears to be more reactive with chlorine so generating larger amounts of THM, a tendency which becomes more accentuated as the MW of the fractions is reduced. Johnson et al. [19] recorded a higher  $\text{UV}_{254}$  for HA fractions between 2 and 10 kDa, indicating a greater presence of aromatic groups. These fractions show notably higher values of SUVA [19] and have been shown to be more reactive in the presence of  $\text{Cl}_2$ , so generating more THM than any other hydrophobic NOM [2]. After ASWUF, there is a reduction in the presence of HA with high MW, while those with lower MW remain in the water and are responsible for the increase in THM generation per gram of DOC. After the coagulation–flocculation/ASWUF combination, the HA fractions remaining in the water are those with the lowest MW, which means that the residual organic matter is even more reactive. In view of this, the results showing reduction of THM after treatment with the coagulation–flocculation/

ASWUF combination need to be viewed with caution, since the residual fraction of NOM in the influent is more reactive and shows higher generation of THM in the presence of disinfectants such as  $\text{Cl}_2$ , which are normally used to maintain safe residuals in long distribution systems.

#### 4. Conclusions

Ultrafiltration systems with ASWUF membranes are not efficient at HA removal, a process affected by the MW of the HA. However, performance is considerably improved when ASWUF is combined with coagulation with  $\text{Cl}_3\text{Fe}$  followed by adequate flocculation. With this combination, values of 90% may be achieved for the removal of HA concentrations of up to 30 mg/l, while problems of membrane fouling and clogging are avoided. At the same time, application of coagulation–flocculation prior to ASWUF treatment makes it possible to retain HA with low molecular weight, without having to modify the pH of the water. This has the effect of decreasing the SUVA value of the effluent and leads to a lower risk of THM generation after post-chlorination, although the HA remaining after treatment generate a higher concentration of THM per unit of DOC. The concentration of the chlorine applied to the water directly affects the generation of THM from the HA. However, the concentration of HA is the most important factor because it determines the demand for chlorine in the water.

#### Acknowledgments

This study was supported by funds from the European Union and the Spanish Ministry of Education and Science (CIT-310200-2005-22). It was conducted at the Institute of Water Research and Department of Civil Engineering of the University of Granada with the collaboration of CADAGUA S.A. and EMASAGRA S.A. The article was translated from Spanish by Julian Bourne of the Faculty of Translation and Interpreting, University of Granada.

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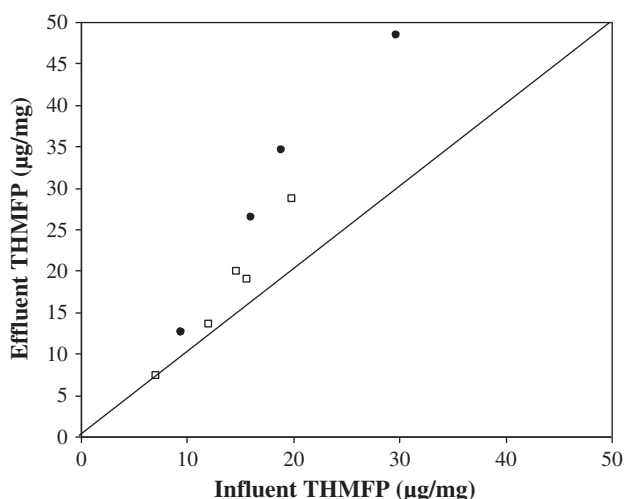


Fig. 7. Effect of treatment on specific THM formation potential (THMP) ( $\mu\text{g THM}/\text{mg DOC}$ ). ASWUF without (□) and with (●) previous coagulation–flocculation.